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Room-temperature effects of UV radiation in KBr:Eu^{2+} crystals

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Abstract. Thermoluminescence and optical absorption measurements have been carried out in KBr:Eu^{2+} crystals irradiated with monochromatic UV light (200–300 nm) and x-rays at room temperature. For UV- and x-irradiated crystals strong similarities between the thermoluminescence glow curves have been found, suggesting that the low-energy UV radiation produces the same defects as produced by x-irradiation in this material. The thermoluminescence glow curves are composed of six glow peaks located at 337, 383, 403, 435, 475 and 509 K. Thermal annealing experiments in previously irradiated crystals show clearly a correlation between the glow peak located at 383 K and the F-centre thermal bleaching process. Also, the excitation spectrum for each thermoluminescence glow peak has been investigated, showing that the low-energy radiation induces the formation of F centres.

1. Introduction

There is a wealth of information about the defect production by ionizing radiation in alkali halide crystals, it being a well known fact that this irradiation produces F centres in pure alkali halide crystals. The defect creation involves a primary electron–hole pair formation giving rise to F and H centres. Some impurity-doped alkali halide crystals show an increase of F-centre production, as compared to non-doped samples, and the F-centre formation efficiency depends on the type of impurity embedded in the crystal (McKeever 1985). In the case of Eu^{2+} -doped NaCl (Rubio *et al* 1982a) and KCl (Rubio *et al* 1982b) the production of F-centres during the first stage coloration by x-irradiation has been found to be proportional to the square root of the Eu^{2+} concentration. These authors have explained the F-centre formation efficiency increase as due to the effect of x-irradiation which reduces the number of isolated Eu^{2+} -cation vacancy dipoles (I–V) and increases the number of trapped electrons, concluding that the I–V dipoles act as the dominant traps for the radiation-induced halogen interstitials.

Additional information about the trapping nature and the possible recombination mechanism processes may be obtained by analysing the thermoluminescence (TL) spectrum. In fact, defect structure induced by ionizing radiation has been successfully studied by TL in conjunction with optical absorption and thermal and optical bleaching methods, in many pure

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and doped alkali halide crystals (McKeever 1985). There is agreement in the sense that the TL emission is due to the recombination of holes (H and V_k centres) and trapped electrons. However, the TL caused in Eu^{2+} -doped alkali halide crystals by non-ionizing radiation (low-energy UV light) has been explained in terms of the photoionization of the Eu^{2+} ion (Aguirre de Cárcer *et al* 1988); afterwards the electrons become trapped, and holes formed as Eu^{3+} recombine with electrons to give rise to the TL emission. In UV- (200–300 nm) irradiated $\text{NaCl}:\text{Eu}^{2+}$ Aguirre de Cárcer *et al* (1991) found that the TL emission spectrum shows a band resembling the characteristic Eu^{2+} emission band, which in turn has been ascribed to the Eu^{2+} electronic transition from the lower excited state $t_{2g}(4f^65d)$ to the ground state ${}^8S_{7/2}(4f^7)$. In addition, the TL excitation spectrum has been reported to consist of a band which coincides with the Eu^{2+} high-energy absorption band (Aguirre de Cárcer *et al* 1991). These facts strongly suggested the participation of the Eu^{2+} ion in the defect formation process through a primary mechanism involving the photoionization of the Eu^{2+} ion. In spite of this evidence there are still some doubts about the photoionization process because the Eu^{3+} ions have not been detected. Further experimental work in $\text{NaCl}:\text{Eu}^{2+}$ irradiated with x-rays and UV light at 80 K (López *et al* 1991) has shown that there is no difference between the TL glow curves: the same TL peaks appear for both types of irradiation. The same phosphor subjected to x-, α , β and UV radiation at room temperature (RT) presents the same TL peak structure independently of the type of irradiation used (Aguirre de Cárcer *et al* 1993), indicating that similar defects are induced by any type of irradiation.

Defect creation by non-ionizing radiation (190–230 nm) in pure KBr crystals irradiated at 80 K has been investigated by analysing the TL excitation spectra of the glow peaks (Kristianpoller and Israeli 1970), suggesting an excitonic-type mechanism as responsible for the defect creation in this material. They found that the TL excitation presents a maximum at 203 nm which coincides with the α absorption band. Use of an extremely sensitive method based on a laser-induced luminescence technique by Sever *et al* (1986) allowed the detection of very low F-centre concentrations in the first stage of coloration. The method permitted the measurement of the F-centre production efficiency of pure KBr irradiated by UV light (180–300 nm) at LNT as a function of the photon energy. The spectral resolved F-centre formation efficiency curve showed two main bands at 188 and 210 nm; the first peak was considered to be due to the exciton absorption tail and we recall that a similar peak was observed by Kristianpoller and Israeli (1970). The 210 nm band has been ascribed to the irradiation effect in the vicinity of the α band (Sever *et al* 1986). The strong correlation between the α band and the F-centre formation efficiency peak suggested the existence of an excitonic-type mechanism involved in the defect creation near a pre-existing anion vacancy, as previously indicated by TL measurements (Kristianpoller and Israeli 1970). F-centre formation by low-energy UV light from 200 to 300 nm in $\text{KCl}:\text{Eu}^{2+}$ irradiated at RT has been recently observed by Aceves *et al* (1994). These authors were able to relate some of the TL glow peaks to the F and F_z centres created by UV radiation. They have also made a comparison with the effects of x-irradiation in $\text{KCl}:\text{Eu}^{2+}$ specimens and concluded that similar products are obtained in UV or x-irradiated samples.

In this work, TL, optical absorption spectra and thermal and optical bleaching have been used to determine the nature of induced defects in $\text{KBr}:\text{Eu}^{2+}$ crystals, which were irradiated at room temperature with monochromatic UV light (200–300 nm) and x-rays. We call attention to the fact that for the non-ionizing low-energy range of excitation, the radiation damage process occurring in the alkali halide (doped and undoped), as well as the trapping and recombination mechanism involving the F-centres is not quite accepted, since the UV energy is not enough to excite interband transitions in the crystal (Aguirre de Cárcer *et al* 1988).

2. Experimental details

The europium-doped KBr crystals were grown by the Czochralski method at the Crystal Growth Laboratory of the Instituto de Física de la Universidad Nacional Autónoma de México (IFUNAM, Mexico). Small pieces of $1 \times 4 \times 4 \text{ mm}^3$, preheated for 30 min at 773 K and then cooled by contact with a metal plate, were exposed at RT to UV monochromatic light and x-rays in the darkness. As a source of x-rays, a Telex-O-Meter (30 kV and $80 \mu\text{A}$) was used. Monochromatic UV light was obtained from a deuterium lamp operating at 30 W coupled to a 0.25 m Kratos monochromator. The light was guided to the planchet of the TL equipment using an optical fibre. TL glow curves were obtained from 300 to 673 K using a Harshaw TLD 4000 system with a linear heating rate of 5 K s^{-1} . Optical absorption measurements were made in the range of 200–850 nm with a Perkin–Elmer $\lambda 9$ spectrophotometer. The spectral TL measurements were made with a modified Harshaw 2000C TLD system, in which the photodetector was replaced by an optical fibre coupled to the entrance slit of an $f/2$ imaging spectrograph (model CP-140, Jobin Yvon). The spectral TL emission was detected with an intensified diode array (PDA model RY700S/RB, Princeton Instruments) placed at the exit slit of the spectrograph. The heating rate used was 5 K s^{-1} .

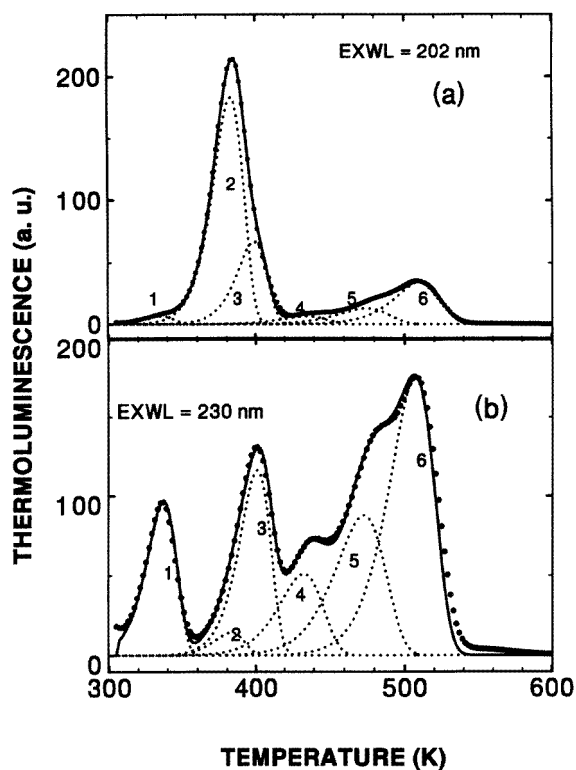


Figure 1. TL glow curves after 120 s irradiation with light of (a) 202 nm and (b) 230 nm. Full and dotted curves are fits, full circles are experimental data points.

3. Results

Figure 1 shows TL glow curves of KBr:Eu²⁺ (150 ppm) crystals obtained after UV irradiation. The glow curves shown in (a) and (b) were obtained immediately after 120 s irradiation with 202 and 230 nm, respectively. The glow curve shown in (a) is a typical one obtained with irradiation wavelengths between 200 and 210 nm, and that in (b) is a characteristic glow curve for irradiation with 210–300 nm light. The main observed feature is the appearance of a high-intensity TL peak around 383 K for relatively high-energy UV irradiation, and its intensity decreases as the energy of the UV irradiation decreases. A similar TL behaviour to that observed in high-energy UV-irradiated samples has been also seen in gamma-irradiated KBr:Eu²⁺ (Buenfil and Brandan 1992). Under gamma irradiation, two main glow peaks were located around 373 and 473 K, it being found that the 373 K is suitable for dosimetric applications. Figure 1 shows also a deconvolution of each TL glow curve; this was done for all the TL glow curves in order to see, after comparison, whether the same peaks appear and to obtain the peak integrated intensity. The deconvolution was performed using first-order kinetic glow peaks, based on the criteria of Chen and Kirsh (1981) and assuming that the TL process involves only isolated luminescent centres. A total of six glow peaks were fitted to each curve (dotted curves numbered 1–6). Their kinetic parameters, activation energy E_a (eV), frequency factor S (s⁻¹) and temperature maximum T_m (K), are all listed in table 1. We remark that the deconvolution method used should be considered as a first approximation, since the TL processes could involve not only a first-order kinetic behaviour.

Table 1. Activation energies E_a , frequency factors S and peak temperatures T_m for the TL glow peaks shown in figure 1.

T_m (K)	E_a (eV)	S (s ⁻¹)
337	0.89	4.45×10^{13}
383	1.01	2.34×10^{13}
403	1.37	3.81×10^{17}
435	1.02	7.56×10^{11}
475	1.09	3.76×10^{11}
509	1.44	2.45×10^{14}

Figure 2(a) displays the defect formation efficiency spectrum for all the glow peaks shown in figure 1, which was obtained by taking the glow peak integrated intensity. Most peaks present a higher integrated TL intensity for shorter wavelength, the 383 and 509 K glow peaks (peaks 2 and 6 in figure 1) being the ones with stronger TL intensity. Figure 2(b) exhibits also the defect formation efficiency spectrum for the total integrated TL intensity (solid curve). The high-energy region of the optical absorption spectrum of the same crystal has also been displayed for comparison. We recall that all spectra were corrected to take into account the characteristic spectral irradiance of the UV light source and the effect of optical fibre light transmission. As observed in figure 2, the TL excitation spectrum presents two main bands located around 204 and 230 nm with a shoulder around 210 nm. It has been reported that the TL excitation spectrum in europium-doped KBr, KCl, KI and NaCl presents an excitation band around 230 nm (Aguirre de Cárcer *et al* 1988); however no evidence was provided for the existence of the bands around 204 and 210 nm as shown in our results. The existence of these TL excitation bands and another one at 187 nm have also been observed in undoped KBr crystals

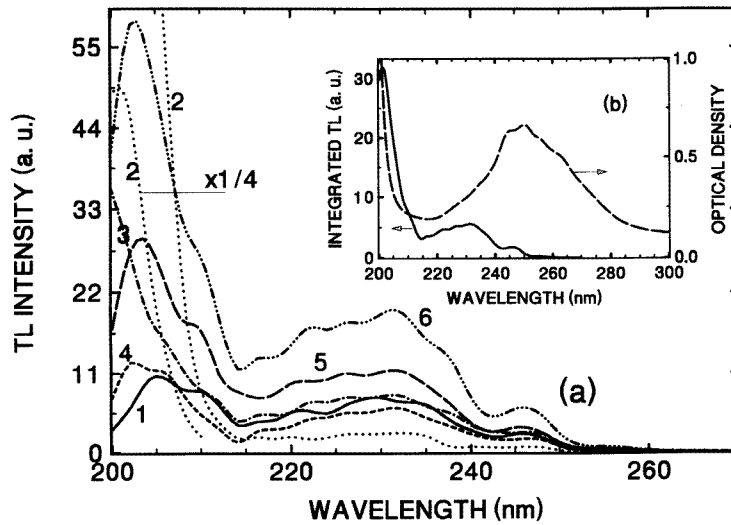


Figure 2. The defect creation spectrum of (a) the integrated TL of each glow peak shown in figure 1 and (b) the integrated TL from 303 up to 600 K (solid curve), and the high-energy region of the optical absorption spectrum (broken curve) of the same crystal.

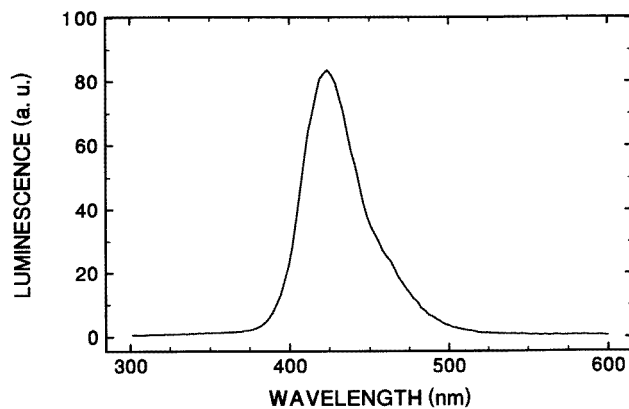


Figure 3. A TL spectrum taken at 400 K during a TL run of a freshly quenched crystal irradiated 30 s with 200 nm light.

subjected to monochromatic UV irradiation (Kristianpoller and Israeli 1970, Sever *et al* 1986).

To obtain more information about the defect recombination during the TL process we have measured the spectral composition of the thermally stimulated luminescence at a rate of 1 spectrum s^{-1} , after 30 s irradiation with light of 200 nm; a spectrum taken around 400 K is displayed in figure 3. In this picture, we recognize the well known Eu²⁺ luminescence bands even though this irradiation light does not correspond to the Eu²⁺ absorption bands. The higher-energy band is associated with the emission of Eu²⁺ belonging to free dipoles and first aggregation products, while the lower-energy band corresponds to Eu²⁺ emission in an EuBr₂-type aggregated phase, as proposed by Aguilar *et al* (1982).

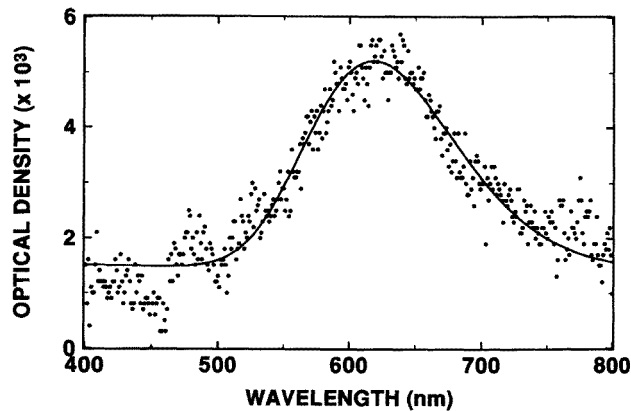


Figure 4. The optical density (full circles) after 7200 s irradiation with 202 nm light. Data fitting was done with a Gaussian curve (full curve).

It is well established that the F centres are produced when pure KBr crystals are exposed to x-rays as well as to UV radiation of wavelength around the excitonic region (Sever *et al* 1986). In this work we have performed some experiments to show also that in KBr:Eu²⁺ crystals at RT the F-centre formation is induced by UV irradiation. Figure 4 shows the optical absorption spectrum in the region of 400–800 nm of a sample irradiated for 2 h with 202 nm light. It presents a broad band centred at 618 nm with a half width of 0.36 eV which is known to be due to the F-centre absorption band in pure KBr crystals (Brown 1967). However no F absorption band was detected in crystals irradiated with light of wavelengths larger than 210 nm. Similar experiments were carried out in pure KBr crystals in order to compare the efficiency of the F-centre formation in Eu²⁺-doped crystals, finding that in KBr:Eu²⁺ the F-centre formation is about 20 times higher than in pure KBr subjected to the same irradiation wavelength under the same condition.

We tried to establish a correlation between the F centres and the TL glow curve induced by irradiation with 202 nm light by examining the thermal annealing of the F centres. The F-centre thermal bleaching experiments were performed by measuring the optical density of the F centres at a fixed wavelength of 624 nm (F band) as a function of time when subjecting the crystal to a linear heating rate ($\sim 2 \text{ K s}^{-1}$) through the 300–493 K range. This procedure allow us to determine the variation of the absorption spectrum as a function of temperature in a very precise way; providing information about the F-centre destruction as a function of temperature. Care was taken to perform both the F-centre annealing and TL experiments at approximately the same heating rate. It was found that under these conditions all measurements were reproducible. It should be mentioned that these experiments were performed separately on the same specimen subjected to the same irradiation and heating conditions. The result of the thermal annealing process is shown in figure 5 (full circles). In order to compare the thermal influence in both processes, a TL glow curve (full curve) of a 120 s UV-irradiated (202 nm) crystal is depicted in the same figure. In figure 5 it may be observed that the annealing of the F centres coincides with the glow peak located at 383 K. On the other hand, photostimulation with F light of 600 nm has been performed in samples previously irradiated with 202 nm. Figure 6 shows the effect of the F light; three TL glow curves are displayed. In all cases the crystal was irradiated for 60 s at 202 nm before

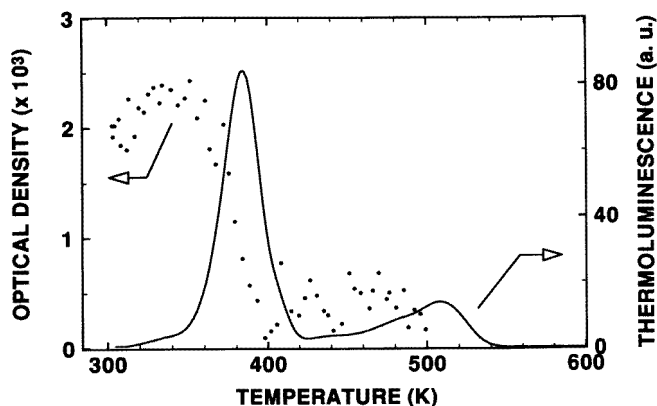


Figure 5. Thermal annealing of F centres measured at 624 nm (full circles), and the TL glow curve obtained after 202 nm irradiation (full curve).

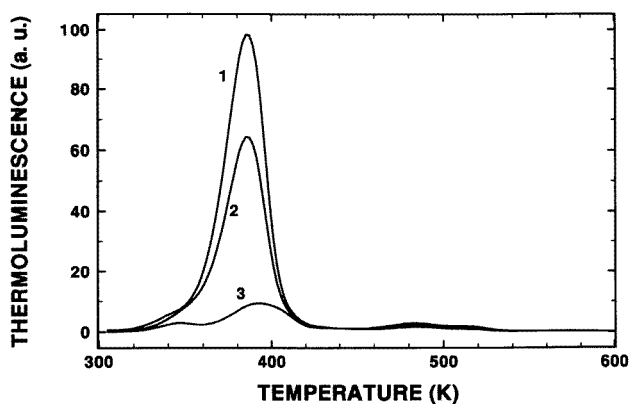


Figure 6. TL glow curves of a 600 nm photostimulated KBr:Eu²⁺ crystal after 60 s irradiation with 202 nm light: 1, $t = 0.0$; 2, $t = 60$ s and 3, $t = 600$ s.

photostimulation. Curve 1 corresponds to the signal induced by the 202 nm irradiation without photostimulation, and curves 2 and 3 present the effect of 60 s and 600 s of photostimulation, respectively. After photostimulation a lower intensity of the 383 K glow peak was observed while the higher-temperature peaks remained approximately constant. This result also provides evidence that the 383 K glow peak is connected to the F-centre destruction.

X-ray irradiation effects on the optical absorption, TL and optical bleaching were compared to those obtained with UV irradiation in KBr:Eu²⁺ crystals. Optical absorption measurements in x-irradiated samples also shows the F band; moreover, the TL glow curves of UV- and x-irradiated samples are almost the same. Figure 7 shows the TL glow curve of a crystal x-irradiated for 5 s (full curve) along with a TL glow curve of the same sample irradiated with 202 nm light (broken curve). The curves were normalized to show the strong similarities in the TL glow peak positions.

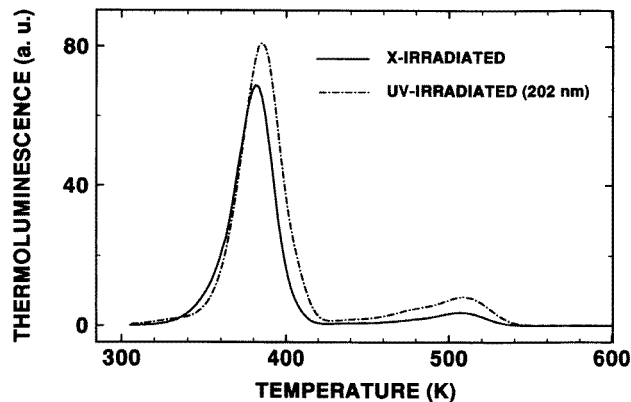


Figure 7. TL glow curves of KBr:Eu²⁺ irradiated with UV light (broken curve) and x-rays (full curve).

4. Discussion and conclusions

TL measurements carried out in UV-irradiated KBr:Eu²⁺ crystals with wavelengths larger than 200 nm indicate that the low-energy UV radiation induces electron–hole pair formation in these crystals. The free holes are apparently captured by different types of trap. In particular, the 383 K glow peak intensity drastically decreases as the irradiation wavelengths increase from 200 to 212 nm, showing that the trap-filling efficiency of this glow peak is strongly dependent on the irradiation energy. The electron–hole pair formation seems evident, since the optical absorption spectrum obtained shows clearly the formation of the F absorption band after irradiation with 202 nm light as well as in x-irradiated crystals, indicating that the electron traps are anion vacancies giving rise to F-centre formation far away from the Eu²⁺-cation vacancy dipoles. If an F centre were created near the I–V dipole, it would be a perturbed F centre by the presence of the dipoles, producing in consequence the characteristic F_z-centre absorption band. It is important to stress the fact that we were not able to detect F_z in our measurements dealing with KBr:Eu²⁺ even at 10 K; we recall that in similar experiments performed in KCl:Eu²⁺, F and F_z centres were observed (Aceves *et al* 1994).

The TL excitation spectrum of figure 2 shows two regions of higher defect formation efficiency, one between 200 and 215 nm and another from 215 to 260 nm. Only the second one of these regions coincides with the Eu²⁺ optical absorption band, which indicates that the first excitation region does not correspond to the Eu²⁺ absorption. Figure 3 gives evidence that irradiating with light in these two regions, the resulting TL luminescence spectrum presents for all the glow peaks the well known Eu²⁺ emissions, which are located around 420 nm in the case of free dipoles or first aggregation products and around 429 and 460 nm in the case of precipitated phases (Rubio 1991). The Eu²⁺ emission after irradiation with 200–215 nm light should not be seen, since it does not belong to the Eu²⁺ absorption region. These emissions can be explained only if the Eu²⁺ ion is indirectly excited after some defect recombination.

On the other hand, the thermal annealing of the F centres shows that they play a fundamental role in the recombination process, mainly around the 383 K glow peak. Taking into account that the energy required to release electrons from the F centres should be at

least of the same order of magnitude as the F-band energy (about 2.0 eV) and that the characteristic activation energy of traps is about 1.0 eV (see table 1, 383 K peak), this implies that just the heating of the sample is not sufficient energy to release electrons from the F centres. This situation led us to consider a recombination process in which the F centre participates as the recombination centre, as proposed by Ausin and Alvarez Rivas (1972). Therefore, the coincidence of the F centre thermal annealing temperature with the 383 K TL glow peak (figure 5) indicates that at 383 K hole detrapping occurs. According to the excitation spectrum of the 383 K glow peak, this peak appears also in crystals irradiated with wavelengths longer than 210 nm, showing that even this low energy induces the F-centre formation with lower efficiency. It is important to notice that 200–300 nm excitation wavelengths produce (see figure 1) the same TL glow curve structure, although with different relative peak intensities, meaning that for any wavelength of irradiation the same products are obtained, which are trapped in six different types of trap. The TL shows that most of the holes obtained when the crystal is irradiated with high-energy irradiation (200–210 nm) participate in the 383 K glow peak and could be related to traps around free dipoles, while the holes generated by low-energy irradiation (210–300 nm) contribute to the emission of the other glow peaks and probably are detrapped from small Eu²⁺ ion aggregates.

The formation efficiency spectrum of the glow peaks 1, 3, 4, 5 and 6 presents two bands located at 204 and 210 nm and another at 230 nm. As in the case of the 204 and 210 nm bands found in pure KBr crystals irradiated at 80 K with 180–230 nm light (Kristianpoller and Israeli 1970, Sever *et al* 1986), these bands can be related to an anion vacancy absorption, since this coincides with the α absorption band in KBr crystals. It is interesting to notice that the 230 nm TL excitation band has not been observed in pure KBr irradiated with monochromatic UV light in the long-wavelength tail of the intrinsic absorption band, so it is plausible to assume that this band may be attributed to a doping impurity-related centre or to an anion ionization effect in the vicinity of small aggregates and not necessarily to the Eu²⁺ ion ionization. However, the experimental evidence provided here is not sufficient to rule out the possibility of the Eu²⁺ photoionization in the defect formation process; further investigation is needed in order to clarify this matter.

In conclusion, we have provided evidence that the 383 K glow peak is associated with F-centre formation in low-energy UV- as well as in x-irradiated KBr:Eu²⁺ crystals at RT, as confirmed by optical absorption, thermal annealing and optical bleaching experiments, indicating the existence of an electron–hole pair recombination process which is responsible for the TL of this peak. On the other hand, it is evident that the origin of the 383 K glow peak is different from that of the other glow peaks, it being possible that the 383 K glow peak could be associated with a particular type of trap surrounding the free dipoles and the others to traps around small aggregates (dimers, trimers, etc) of europium ions. Further research is under way in order to clarify the hole nature, the trapping entities and the recombination mechanisms.

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